



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Re: Application of Jacobsen et al.

Serial No: 10/523,828

Filed: 02/08/2005

For: SUPPORTED POLYMERISATION CATALYSTS

DECLARATION OF STEFAN KLAUS SPITZMESSER

I, Stefan Klaus Spitzmesser, do hereby solemnly declare as follows:-

1. I am a German subject, residing at Avenue J.R. Collon 12, 1200 Brussels, Belgium.
2. I am familiar with the technical details concerning the US Patent Application Serial No. 10/523,828 filed on 8<sup>th</sup> February 2005.
3. In the Office Action dated March 12<sup>th</sup> 2007, the Examiner has maintained that the claims of the present invention are obvious over US Patents 5,783,512 and 6,271,165, hereinafter D1 and D2 respectively, and that the evidence provided previously could not overcome the objection because of differences in the catalyst preparation between the comparative and inventive examples therein.
4. The attached Appendix 2 presents further data, this time from comparative and inventive examples in which the only difference between the catalysts is the use of tetraisobutylaluminumoxane (invention) instead of triethylaluminium (comparative). Both catalysts are then used for polymerisation under identical conditions.
5. Consistent with earlier results, and with the statements in the application as filed, the new results in Appendix 2 again show the advantageous activity profile from the catalysts according to the present invention, and in particular, that the initial exotherm from the use of an aluminoxane compared to an alkylaluminium is much lower.

All statements made of my own knowledge are true and all statements made on information and belief are believed to be true. I also understand that willful false statements and the like are punishable by fine or imprisonment, or both (18 U.S.C. 1001) and may jeopardize the validity of the application or any patent issuing thereon.

Signed:

Date:

09/07/2007

STEFAN KLAUS SPITZMESSER

## Appendix 2

### Comparative catalyst preparation

#### (i) Treatment of silica

A suspension of Grace 948 silica (10kg, previously calcined at 250°C for 5 hours) in 110 litres (L) of hexane was made up in a 240L vessel under nitrogen. 1L of a hexane solution containing 2g/L of Stadis 425 was added and stirred at room temperature for 5 minutes. 35.6L of a 1molAl/L solution of triethylaluminium (TEA) in hexane was added slowly to the stirred suspension over 30 minutes, while maintaining the temperature of the suspension at 30°C. The suspension was stirred for a further 1 hour. The hexane was filtered, and the silica washed with hexane, so that the aluminium content in the final washing was less than 0.5 mmol Al/litre. Finally the suspension was dried *in vacuo* at 60°C to give a free flowing treated silica powder with residual solvent less than 0.5wt%.

#### (ii) Catalyst fabrication – Invention

All steps, unless otherwise stated, of the catalyst fabrication were carried out at 20°C. 2.26ml of a 10.54wt% solution in toluene of bis(hydrogenated tallow alkyl) methyl ammonium tris(pentafluorophenyl)(4-hydroxyphenyl)borate was reacted for 15 minutes with 0.21ml of a 850mmolAl/L solution in cyclohexane of tetraisobutylaluminumoxane.

2.47 ml of this solution was slowly impregnated to 3.0g of the TEA treated silica described above and manually agitated until no lumps were visible. The mixture of TEA treated silica and solution was held for 30 minutes.

0.75ml of 1-hexene was then slowly impregnated to the TEA treated silica and manually agitated until no lumps were visible. The mixture of TEA treated silica and 1-hexene was held for 30 minutes.

0.83ml of a 10.55wt% solution in heptane of (t-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl) dimethylsilane titanium -  $\eta^4$ -1,3-pentadiene was slowly impregnated to the TEA treated silica and manually agitated until no lumps were visible. The mixture of TEA treated silica and solution was held for 30 minutes. Then the catalyst was dried *in vacuo*.

#### (iii) Catalyst fabrication - Comparative

All steps, unless otherwise stated, of the catalyst fabrication were carried out at 20°C. 2.32ml of a 10.54wt% solution in toluene of bis(hydrogenated tallow alkyl)

methyl ammonium tris(pentafluorophenyl)(4-hydroxyphenyl)borate was reacted for 15 minutes with 0.75ml of a 250mmolAl/L solution in hexane of triethylaluminium.

3.07 ml of this solution was slowly impregnated to 3.0g of the TEA treated silica described above and manually agitated until no lumps were visible. The mixture of TEA treated silica and solution was held for 30 minutes.

0.78ml of 1-hexene was then slowly impregnated to the TEA treated silica and manually agitated until no lumps were visible. The mixture of TEA treated silica and 1-hexene was held for 30 minutes.

0.87ml of a 10.55wt% solution in heptane of (t-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl) dimethylsilanetitanium - $\eta^4$ -1,3-pentadiene was slowly impregnated to the TEA treated silica and manually agitated until no lumps were visible. The mixture of TEA treated silica and solution was held for 30 minutes. Then the catalyst was dried *in vacuo*.

### Experimental

The two catalysts produced above were tested under identical conditions for copolymerisation of ethylene and 1-hexene as follows:

A 2.5L double jacketed thermostatic stainless steel autoclave was purged with nitrogen at 70°C for at least one hour. 150g of PE pellets previously dried under vacuum at 80°C for 12 hours were introduced and the reactor was then purged three times with nitrogen (7 bar to atmospheric pressure).  $\approx 0.1$  g of TEA treated silica (1.5 mmol TEA/g) was added under pressure and allowed to scavenge impurities for at least 15 minutes under agitation. The gas phase was then composed (addition of ethylene, 1-hexene and hydrogen) and a mixture of supported catalyst ( $\approx 0.1$  g) and silica/TEA ( $\approx 0.05$  g) was injected. A constant pressure of ethylene and a constant flowrate ratio of ethylene/comonomer were maintained during the run. The run was terminated by venting the reactor and then purging the reactor three times with nitrogen. The PE powder produced during the run was then separated from the PE seed bed by simple sieving.

Typical conditions are as follows:

Temperature: 70°C

Ethylene pressure: 6.5 bar

Flowrate (1-hexene)/Flowrate (ethylene): 0.096

Hydrogen: 80 ml added during the gas phase composition

The reaction profile of the comparative catalyst is shown as A in Figure 1 below and compared to the catalyst according to the present invention, which is shown as B.

The increase in activity profile shown initially is directly related to the reaction exotherm. It can be seen that the exotherm with the Example according to the present invention (B) is significantly lower than that observed for the equivalent reaction using the comparative catalyst (A). This would be expected to result in an improvement of the operability of the catalyst at industrial scale.

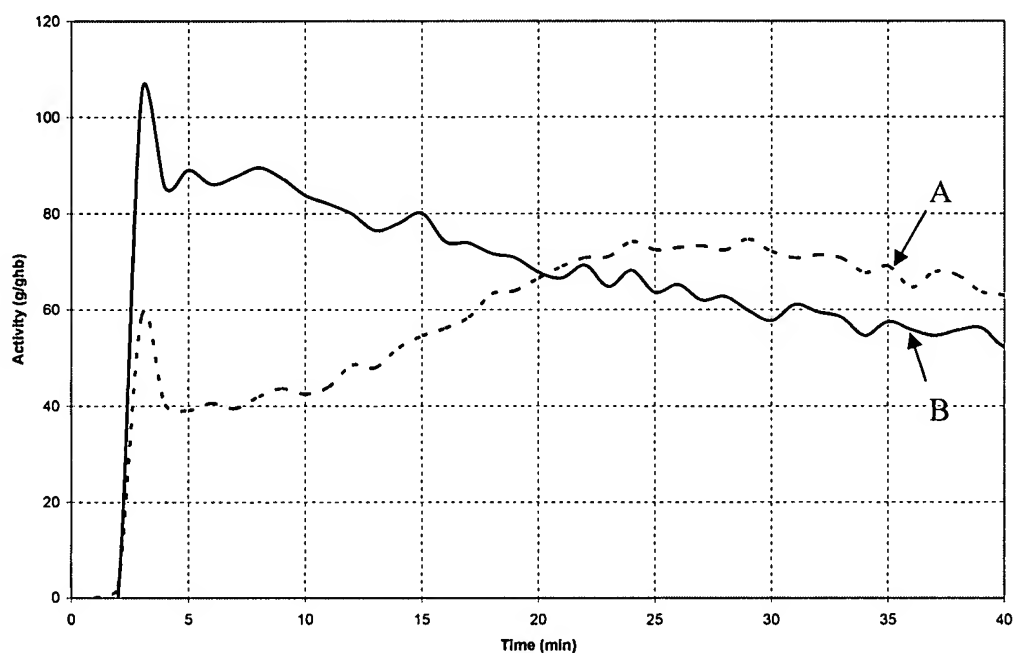


Fig1: Activity profiles